

EFFICIENT AND ENVIRONMENTALLY FRIENDLY INK-JET PRINTING OF ELECTROCERAMIC THIN FILMS OF TiO₂ AND TITANATES

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Abstract. *In this work, aqueous chemical solution deposition precursors suited for inkjet printing, are used for the synthesis of photocatalytically active TiO₂ coatings and BaTiO₃ thin films. Environmentally friendly precursor solutions with electromagnetic ink-jet printing, allows cheap and simple processing of TiO₂ films on glass and BaTiO₃ films on LSMO substrates. The hydrolysis reaction of water sensitive titanium alkoxide (Ti-alkoxide) precursor is controlled by adding complexing agents such as citric acid and triethanolamine, and aqueous stable solutions are achieved. The pH of the solutions is brought to neutral to guarantee flexible processing and avoid damage to substrates and equipment. Ba²⁺ ions are stabilized by using citric acid, ethyleneglycol, and nitrilotriacetic acid, and BaTiO₃ solutions are prepared by mixing separate Ba- and Ti- precursor solutions at the same pH levels. Solution parameters are adapted to obtain optimal gelation conditions and good jettability. The influence of processing parameters on the phase formation and surface morphology is studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The photocatalytic activity of the TiO₂ films is evaluated by the degradation of methyl orange.*

1 INTRODUCTION

Ceramic, functional and patterned coatings are required for innovations in communication, electronics, energy technology and catalysis. Especially in thin layers and coatings these material properties can be specifically tailored for use in innovative applications and/or give added value to existing products [1, 2].

The objective of this study is to develop a cost-effective and environmentally friendly synthesis using soft chemistry based on Chemical Solution Deposition (CSD). The main advantages are the lower investment, the faster deposition with higher yield and the processing under ambient pressure enabling a complete continuous processing. The materials chosen for this study are TiO_2 and BaTiO_3 in view of the different sectors in electroceramics. TiO_2 will be developed for photocatalytic layers and (Ba) titanate for specific photonic applications and multiferroics. Preparation of these materials at lower temperatures without using toxic substances or organic solvents is new in this area.

TiO_2 and BaTiO_3 films prepared by chemical solution deposition methods are used for relatively simple production of large area, high purity films at low cost and high scalability [3]. We want to avoid precipitation by blocking the hydrolysis reaction in pure aqueous media, using complexing ligands as stabilizing agents such as triethanolamine (TEA) and citric acid (CA). There are a limited number of publications on aqueous TiO_2 solutions starting from alkoxides such as the study of Ohya et al. where different complexing agents were used to create precursor solutions suited for spincoating on glass [4]. In most studies, very low pH values were applied [5, 6], which is unfavorable, since this complicates further industrial handling, can damage the substrate, and might influence phase formation. Some studies describe the use of highly corrosive peroxide [7, 8]. In this study, we focus on fast, economically synthesized, and completely environmentally friendly solutions by eliminating toxic organics. BaTiO_3 films in multiferroic systems consist of a ferroelectric and a ferromagnetic layer, which interact at the interface in that way, that an applied electric field in the ferroelectric layer induces a change of magnetisation in the ferromagnetic layer. BaTiO_3 (BTO) is ferroelectric crystal with to its outstanding dielectric and ferroelectric properties [9]. BaTiO_3 films prepared by sol-gel technique are attracting great interest due to low temperature processing, chemical homogeneity, uniform deposition, low equipment cost, and easy integration with the current semiconductor technology. Electrical characterisation of ferroelectric BTO films requires an electric conducting substrate. Therefore, in this study the intention is to grow a heterostructure with LSMO acting as a ferromagnetic ground layer and simultaneously acting as an electric contact to the bottom electrode followed by the ferroelectric BTO layer on top.

To apply these solutions to the substrate, we have shifted from the common techniques to a new approach, ink-jet printing. This is a non-contact deposition method used to obtain large area coverage by generating droplets of precursor solution in selected pattern on almost any substrate [10]. In this way, both patterned deposits and completely covered surfaces can be obtained, resulting in simplicity, low cost, less material waste, and convenient coating control.

This study focuses on preparing water based stable precursors at neutral pH and with simple complexing agents, inkjet printing the TiO_2 solutions on glass and BaTiO_3 solution on LSMO

substrates, and sintering at low temperatures to transform the wet printed layers to the final crystalline and dense layers.

2 EXPERIMENTAL PROCEDURE

Aqueous TiO_2 precursor solutions were prepared using tetrabutyl orthotitanate (TNBT) (Fluka, $\geq 97.0\%$ from) as Ti^{4+} source, citric acid (CA) (Acros Organics, 99.5%) and triethanolamine (TEA) (Acros Organics, 99+%) as complexing agents, and small amounts of ethanol (EtOH) (Absolute, Panreac). Aqueous BaTiO_3 solutions were prepared using identical chemicals for TiO_2 solution, and also additional Barium acetate ($\text{Ba}(\text{OAc})_2$) ($\geq 99.0\%$) as Ba source, nitrilotriacetic acid (NTA) ($\geq 99.0\%$), ethanolamine (EA) ($\geq 99.0\%$), ethyleneglycol (EG) ($\geq 99.5\%$) from Sigma-Aldrich. All materials were used without further purification.

Two different TiO_2 precursor solutions were prepared with CA and TEA as complexing agents, and water as the primary solvent as reported elsewhere [11]. Briefly, Ti-CA solution was prepared by dissolving TNBT in small amount of EtOH, mixing CA in 2:1 molar ratio to Ti^{4+} at 60°C , and adding H_2O in 82:1 molar ratio in order obtain a final Ti^{4+} concentration of 0.4 M. Ti-TEA solution was prepared by adding TEA to TNBT in molar ratio of 2:1 and H_2O in 71:1 molar ratio, and stirring at 40°C to obtain a final Ti^{4+} concentration of 0.5 M. For solution Ti-CA, pH adjustment to 5.5 was done by adding NH_4OH (NH_3 in 25 wt% water). The pH of solution Ti-TEA was 9 and the precursor was used as such.

Ba- precursor solutions were prepared by using different complexing agents. For the first solution, $\text{Ba}(\text{OAc})_2$ was dissolved in H_2O , EG and CA was added. In the second solution NTA with the addition of EA (to increase pH) was used to stabilize Ba^{2+} ions. Throughout this paper, these solutions are named respectively as B1 and B2. To obtain a stable BaTiO_3 solution, prepared Ti-TEA precursor solution and Ba- precursors were mixed separately at the same pH level and the right stoichiometry with a final concentration of 0.25M.

For inkjet printing of TiO_2 precursor solutions, a single Domino Macrojet electromagnetic nozzle with 90 μm diameter jewel orifice, modified in-house and mounted on a Roland x-y plotter was used. The pressure was set between 0.3-0.8 bar and the deposition was performed at room temperature. The glass substrates used for coating were standard microscope slides with dimensions 20×50 mm. Interdroplet distance was varied between 2 and 5 mm to obtain optimum substrate coverage, and the droplets had diameters of ≤ 1 mm after spreading on the substrate. After printing the layers were gelled at 60°C for 3-4 h under air. Sintering was performed in a tube furnace at 500-650 $^\circ\text{C}$ for 1h with a heating rate of 5 $^\circ\text{C}/\text{min}$ in air.

BaTiO_3 precursors were printed on LSMO substrates by Sonoplot GIX Microplotter. The advantage of this system is the spraying of the fluid on top of the substrate compared to ink-jet printing of a multi nozzle system, where the ink drops on top of the surface. By using a very thin glass needle with a diameter of only 10 μm for the plotting process very thin BTO films were prepared. Subsequent annealing was done in a tube furnace up to crystallisation temperatures of 750 $^\circ\text{C}$ in air.

The viscosity of the solutions was determined using a Brookfield DVE viscometer. The wettability was studied by measuring the contact angle of a 10 μl droplet of precursor solution on glass substrates, and the surface tension by the pendant drop method using an optical

tensiometer (KSV CAM 200). XRD analysis was performed by using Lynxeye line detector, 0.04° step size, and 2 sec step time (Bruker D8, Cu K α radiation) to check the crystal structure. The homogeneity and smoothness of the films was investigated by SEM (FEI Quanta 200F) and AFM (Molecular Imaging, PicoPlus). The thickness of the films was measured by a spectroscopic ellipsometer (SE, J.A. Woollam Co. Inc., M-2000FI) where the Cauchy dispersion model was used to fit the optical constants. The photocatalytic activity of the TiO₂ films was evaluated by following the degradation of methyl orange under UV illumination. The experiments were carried out in round-bottom photocatalytic cells with a near UV-transparent window. The photon source had a maximum emission at 360 nm and emits $71.7 \mu\text{W cm}^{-1}$ at a distance of 25 cm. The titania modified microscopy slides were accurately shaped at 2.0 cm^2 and inserted in the photocatalytic cell and stirred as 25 cm of the light source.

3 RESULTS AND DISCUSSION

We have prepared different aqueous TiO₂ and BaTiO₃ precursor solutions by using citric acid (CA) and triethanolamine (TEA), ethyleneglycol (EG), and nitrilotriacetic acid (NTA) as complexing agents, to inhibit hydrolysis of the Ti-alkoxide and Ba-acetate. When stored in sealed beakers at room temperature, the solutions were stable for several months. This stability is of major importance to the suitability for ink-jet printing: formation of even very small precipitates can block the nozzles. Heating of small amount of the solutions poured into a petri dish to 60°C for 2 hours has lead to stable and transparent gels.

BaTiO₃ films were deposited by ink plotting using a $10 \mu\text{m}$ diameter glass needle. An assembly of droplets of BTO solutions can cover the LSMO substrate in an area of $1 \times 1 \text{ mm}$, leading to a very thin BTO film with a homogeneous thickness. By subsequent annealing in a tube furnace up to crystallisation temperatures of 750°C in air, very thin but crack free BTO layers have been prepared. BTO films with cracks are absolutely inadmissible in ferroelectric films.

For TiO₂ solutions, the ink-jet printing parameters were chosen according to the rheological properties of the solutions (Table 1). The opening time determined the size of each droplet printed on the substrate and was kept constant at an optimized value. Both solutions could be printed successfully on glass substrates without the addition of any wetting agent. Good spreading and adherence of the droplets on the glass surfaces was achieved. A lower ink supply pressure needed to be used in order to print good layers for solution Ti-TEA in comparison with solution Ti-CA, as the viscosity of solution Ti-TEA is higher than that of solution Ti-CA, as shown in Table 1. From contact angle measurement we found that droplets of solution Ti-CA and Ti-TEA spread completely on the glass substrates. Compared to the surface tension of water, which is 72 mN/m , our solutions have a lower surface tension (Table 1) which explains why the droplets spread easily to form a complete layer on the substrate.

Solution	Viscosity [cP]	Contact Angle [$^\circ$]	Surface Tension [mN/m]	IJP Pressure [bar]	IJP Opening Time [μs]	Distance Between Droplets [mm]
Ti-CA	4.3	≤ 5	24.6	0.4	100	5
Ti-TEA	5.2	≤ 5	25.3	0.3	50	2

Table 1. Ink-jet printing (IJP) parameters with rheological properties of the TiO₂ solutions.

After printing and drying, the TiO₂ films were heated in air at 500-650°C. Both powders obtained by sintering the prepared solutions and films were analyzed by XRD (Fig. 1). All TiO₂ powders and films were crystalline. At 500°C, pure anatase phase was formed for both powders and films (Fig. 1a, 1b). The wider peak width for Ti-TEA powder indicates smaller grain size which is in line with the morphology of the films that will be discussed later. When the sintering temperature is increased up to 650°C, a small amount of rutile phase was detected for the Ti-CA layer (Fig. 1c).

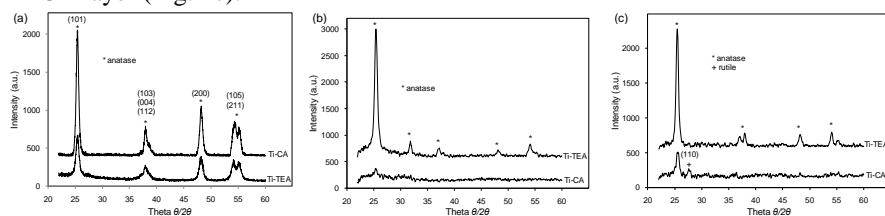


Figure 1: XRD patterns of the TiO₂ (a) powders, (b) thin films sintered at 500°C for 1h, (c) thin films sintered at 650°C for 1h, prepared from aqueous solutions Ti-CA and Ti-TEA.

SEM analysis was performed on the sintered TiO₂ layers under low vacuum (Fig. 2). In the case of the layer from solution Ti-CA, larger and more elongated grains were present in between more round shaped grains, and their concentration and size seemed to increase further with temperature. The TiO₂ layers obtained from solution Ti-TEA exhibited a smoother and a porous surface. The surface roughness of both films appeared to increase with temperature.

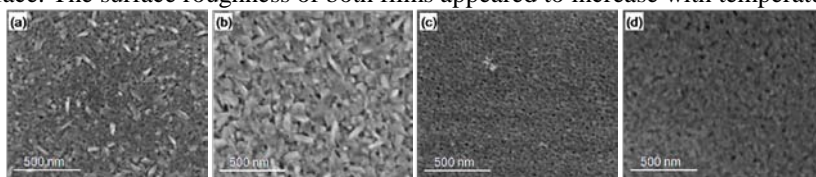


Figure 2: SEM micrographs of surfaces of different TiO₂ films on glass prepared from solution Ti-CA sintered for 1h at (a) 500°C, (b) 600°C and from solution Ti-TEA sintered for 1 h at (c) 500°C, (d) 600°C.

In order to determine the grain size and roughness of the films, non-contact AFM measurements were performed. For TiO₂ films sintered at 500°C, the grain size was estimated at 90-100 nm for Ti-CA and 45-50 nm for Ti-TEA films. The RMS surface roughness measured on an area of 5.0 $\mu\text{m} \times 5.0 \mu\text{m}$, was 6.6 nm for the Ti-CA film and 2.5 nm for the Ti-TEA film. When the sintering temperature was increased, the grain size increased, and the surface roughness rose to 7.6 nm for the Ti-CA film and 3.9 nm for the Ti-TEA film.

From ellipsometry, a layer thickness of ± 85 nm for Ti-CA, ± 600 nm for Ti-TEA film, is found, and compared to commercial self-cleaning window glass from Saint-Gobain (SGG Bioclean) which had ± 50 nm thickness. The different results in terms of layer thickness, relate

to the different characteristics of the precursor solutions (see Table 1). In the case of Ti-TEA, a much larger volume of precursor solution per area can be printed due to considerable differences in rheology, wetting and spreading behavior.

The photocatalytic activity of the TiO_2 films was compared with a reference sample film of Degussa P25 made by doctor blade coating and a sample of commercially available SGG Bioclean. The photocatalytic decomposition of methyl orange is studied as a function of time by measuring the change in the absorbance under UV illumination. The photocatalytic process follows a pseudo first-order kinetic mechanism: [12]

$$\ln(C/C_0) = -kt \quad (1)$$

Where C is the concentration of methyl orange after photocatalysis time t , C_0 is the initial methyl orange concentration, and k is the kinetic constant of the reaction. The kinetic constants k of photocatalysis were found to be $k_{\text{CA}} = 3,01 \cdot 10^{-4} \pm 0,02 \cdot 10^{-4} \text{ min}^{-1}$ for Ti-CA film and $k_{\text{TEA}} = 4,70 \cdot 10^{-4} \pm 0,03 \cdot 10^{-4} \text{ min}^{-1}$ for Ti-TEA film. It can be seen in Figure 3 that increased thickness of titania films supports better photocatalytic efficiency (Ti-TEA). Yet, we also found that the Ti-TEA film exhibits a lower roughness and smaller grain size than the Ti-CA films. Smaller grain size means higher active surface and thus better photocatalytic activity. In Fig. 3, Ti-TEA films and a commercial SGG Bioclean glass which is known as coated by chemical solution derived, transparent, and photocatalytically active layer, were compared. Both show a higher activity which might be related to a large difference in thickness between the layers. Ti-TEA layers are $> 500 \text{ nm}$ thick while typically, the SGG layer is only 50 nm thick.

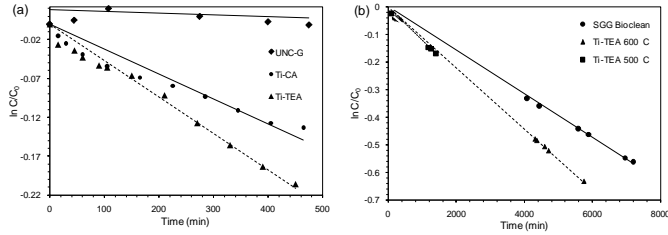


Figure 3: Kinetics of the photocatalytic degradation of methyl orange using (a) uncoated (UNC-G) and TiO_2 coated (sintered at 500°C) glass and (b) commercial Saint-Gobain titania coated glass and TiO_2 films derived from Ti-TEA precursor sintered at 500°C and 600°C .

For the BTO layers, AFM measurements reveal a very small grain size in particular BTO layer prepared from B2-Ti solution, as seen in figure 4. The BTO layer thickness was measured to be about 20 nm in both films.

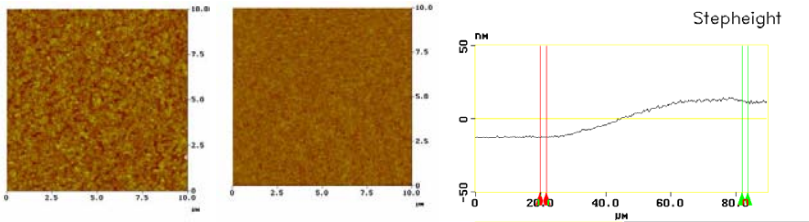


Figure 4: AFM measurements of BTO films after heat treatment prepared by ink plotting from a) B1-Ti solution and b) B2-Ti solution.

The crack formation in the BTO layers can be avoided by very slow heating rate (60 K/h) during pyrolysis and crystallization. To obtain thicker films, the coating-annealing process was repeated several times. In order to perform the electrical characterisation a liquid silver contact was deposited on top of a double BTO layer. The polarisation and corresponding displacement were recorded as a function of applied voltage. Polarisation hysteresis loops could be successfully measured at room temperature. A decrease of the saturation polarization at large voltages was observed, which is supposed to be originated of a leakage current obscuring the switching (displacement) process. Another assumption for the decrease of the saturation polarisation is the influence of the rough surface of the BTO layers as a consequence of the deposition method.

4 CONCLUSION

Homogeneous, transparent, and thin TiO_2 and BaTiO_3 films have been obtained by a chemical solution deposition method using water as the primary solvent and non-toxic substances such as citric acid and triethanolamine, ethyleneglycol, nitrilotriacetic acid as stabilizing agents. These water based and environmentally friendly solutions can be deposited on substrates by ink-jet printing, which is a new technique allowing cheap and fast deposition and avoiding material waste.

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